

## Environmental Protection Agency

## Pt. 60, App. A-6, Meth. 16A

12.4 Concentration of Recovery Gas Generated in the System Performance Check.

$$C_{RG} = \frac{Q_{H_2S} C_{H_2S}}{Q_{H_2S} + Q_{CG}} \quad \text{Eq. 16A-3}$$

12.5 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{RG(m)}}{C_{RG(act)}} \times 100 \quad \text{Eq. 16A-4}$$

### 13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv SO<sub>2</sub> when sampling at 2 liters/min (4.2 ft<sup>3</sup>/hr) for 3 hours or 0.3 ppmv when sampling at 2 liters/min (4.2 ft<sup>3</sup>/hr) for 1 hour. The upper concentration limit of the method exceeds the TRS levels generally encountered at kraft pulp mills.

13.2 Precision. Relative standard deviations of 2.0 and 2.6 percent were obtained when sampling a recovery boiler for 1 and 3 hours, respectively.

#### 13.3 Bias.

13.3.1 No bias was found in Method 16A relative to Method 16 in a separate study at a recovery boiler.

13.3.2 Comparison of Method 16A with Method 16 at a lime kiln indicated that there was no bias in Method 16A. However, instability of the source emissions adversely affected the comparison. The precision of Method 16A at the lime kiln was similar to that obtained at the recovery boiler (Section 13.2.1).

13.3.3 Relative standard deviations of 2.7 and 7.7 percent have been obtained for system performance checks.

### 14.0 Pollution Prevention. [Reserved]

### 15.0 Waste Management. [Reserved]

### 16.0 Alternative Procedures

As an alternative to the procedures specified in Section 7.1.4, the following procedure may be used to verify the H<sub>2</sub>S concentration of the recovery check gas.

16.1 Summary. The H<sub>2</sub>S is collected from the calibration gas cylinder and is absorbed in zinc acetate solution to form zinc sulfide. The latter compound is then measured iodometrically.

16.2 Range. The procedure has been examined in the range of 5 to 1500 ppmv.

16.3 Interferences. There are no known interferences to this procedure when used to analyze cylinder gases containing H<sub>2</sub>S in nitrogen.

16.4 Precision and Bias. Laboratory tests have shown a relative standard deviation of less than 3 percent. The procedure showed no bias when compared to a gas

chromatographic method that used gravimetrically certified permeation tubes for calibration.

#### 16.5 Equipment and Supplies.

16.5.1 Sampling Apparatus. The sampling train is shown in Figure 16A-4. Its component parts are discussed in Sections 16.5.1.1 through 16.5.2.

16.5.1.1 Sampling Line. Teflon tubing (¼-in.) to connect the cylinder regulator to the sampling valve.

16.5.1.2 Needle Valve. Stainless steel or Teflon needle valve to control the flow rate of gases to the impingers.

16.5.1.3 Impingers. Three impingers of approximately 100-ml capacity, constructed to permit the addition of reagents through the gas inlet stem. The impingers shall be connected in series with leak-free glass or Teflon connectors. The impinger bottoms have a standard 24/25 ground-glass fitting. The stems are from standard 6.4-mm (¼-in.) ball joint midget impingers, custom lengthened by about 1 in. When fitted together, the stem end should be approximately 1.27 cm (½ in.) from the bottom (Southern Scientific, Inc., Micanopy, Florida: Set Number S6962-048). The third in-line impinger acts as a drop-out bottle.

16.5.1.4 Drying Tube, Rate Meter, and Barometer. Same as Method 11, Sections 6.1.5, 6.1.8, and 6.1.10, respectively.

16.5.1.5 Cylinder Gas Regulator. Stainless steel, to reduce the pressure of the gas stream entering the Teflon sampling line to a safe level.

16.5.1.6 Soap Bubble Meter. Calibrated for 100 and 500 ml, or two separate bubble meters.

16.5.1.7 Critical Orifice. For volume and rate measurements. The critical orifice may be fabricated according to Section 16.7.3 and must be calibrated as specified in Section 16.12.4.

16.5.1.8 Graduated Cylinder. 50-ml size.

16.5.1.9 Volumetric Flask. 1-liter size.

16.5.1.10 Volumetric Pipette. 15-ml size.

16.5.1.11 Vacuum Gauge. Minimum 20 in. Hg capacity.

16.5.1.12 Stopwatch.

16.5.2 Sample Recovery and Analysis.

16.5.2.1 Erlenmeyer Flasks. 125- and 250-ml sizes.

16.5.2.2 Pipettes. 2-, 10-, 20-, and 100-ml volumetric.

16.5.2.3 Burette. 50-ml size.

16.5.2.4 Volumetric Flask. 1-liter size.

16.5.2.5 Graduated Cylinder. 50-ml size.

16.5.2.6 Wash Bottle.

16.5.2.7 Stirring Plate and Bars.

16.6 Reagents and Standards. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

16.6.1 Water. Same as Method 11, Section 7.1.3.

16.6.2 Zinc Acetate Absorbing Solution. Dissolve 20 g zinc acetate in water, and dilute to 1 liter.

16.6.3 Potassium Bi-iodate [ $\text{KH}(\text{IO}_3)_2$ ] Solution, Standard 0.100 N. Dissolve 3.249 g anhydrous  $\text{KH}(\text{IO}_3)_2$  in water, and dilute to 1 liter.

16.6.4 Sodium Thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) Solution, Standard 0.1 N. Same as Method 11, Section 7.3.2. Standardize according to Section 16.12.2.

16.6.5  $\text{Na}_2\text{S}_2\text{O}_3$  Solution, Standard 0.01 N. Pipette 100.0 ml of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution into a 1-liter volumetric flask, and dilute to the mark with water.

16.6.6 Iodine Solution, 0.1 N. Same as Method 11, Section 7.2.3.

16.6.7 Standard Iodine Solution, 0.01 N. Same as in Method 11, Section 7.2.4. Standardize according to Section 16.12.3.

16.6.8 Hydrochloric Acid (HCl) Solution, 10 Percent by Weight. Add 230 ml concentrated HCl (specific gravity 1.19) to 770 ml water.

16.6.9 Starch Indicator Solution. To 5 g starch (potato, arrowroot, or soluble), add a little cold water, and grind in a mortar to a thin paste. Pour into 1 liter of boiling water, stir, and let settle overnight. Use the clear supernatant. Preserve with 1.25 g salicylic acid, 4 g zinc chloride, or a combination of 4 g sodium propionate and 2 g sodium azide per liter of starch solution. Some commercial starch substitutes are satisfactory.

#### 16.7 Pre-test Procedures.

16.7.1 Selection of Gas Sample Volumes. This procedure has been validated for estimating the volume of cylinder gas sample needed when the  $\text{H}_2\text{S}$  concentration is in the range of 5 to 1500 ppmv. The sample volume ranges were selected in order to ensure a 35 to 60 percent consumption of the 20 ml of 0.01 N iodine (thus ensuring a 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  titer

of approximately 7 to 12 ml). The sample volumes for various  $\text{H}_2\text{S}$  concentrations can be estimated by dividing the approximate ppm-liters desired for a given concentration range by the  $\text{H}_2\text{S}$  concentration stated by the manufacturer. For example, for analyzing a cylinder gas containing approximately 10 ppmv  $\text{H}_2\text{S}$ , the optimum sample volume is 65 liters (650 ppm-liters/10 ppmv). For analyzing a cylinder gas containing approximately 1000 ppmv  $\text{H}_2\text{S}$ , the optimum sample volume is 1 liter (1000 ppm-liters/1000 ppmv).

Approximate cylinder gas $\text{H}_2\text{S}$ concentration (ppmv)	Approximate ppm-liters desired
5 to <30 .....	650
30 to <500 .....	800
500 to <1500 .....	1000

16.7.2 Critical Orifice Flow Rate Selection. The following table shows the ranges of sample flow rates that are desirable in order to ensure capture of  $\text{H}_2\text{S}$  in the impinger solution. Slight deviations from these ranges will not have an impact on measured concentrations.

Cylinder gas $\text{H}_2\text{S}$ concentration (ppmv)	Critical orifice flow rate (ml/min)
5 to 50 ppmv .....	1500 $\pm$ 500
50 to 250 ppmv .....	500 $\pm$ 250
250 to <1000 ppmv .....	200 $\pm$ 50
>1000 ppmv .....	75 $\pm$ 25

16.7.3 Critical Orifice Fabrication. Critical orifice of desired flow rates may be fabricated by selecting an orifice tube of desired length and connecting  $\frac{1}{16}$ -in. x  $\frac{1}{4}$ -in. (0.16 cm x 0.64 cm) reducing fittings to both ends. The inside diameters and lengths of orifice tubes needed to obtain specific flow rates are shown below.

Tube (in. OD)	Tube (in. ID)	Length (in.)	Flowrate (ml/min)	Altech Catalog No.
$\frac{1}{16}$ .....	0.007	1.2	85	301430
$\frac{1}{16}$ .....	0.01	3.2	215	300530
$\frac{1}{16}$ .....	0.01	1.2	350	300530
$\frac{1}{16}$ .....	0.02	1.2	1400	300230

16.7.4 Determination of Critical Orifice Approximate Flow Rate. Connect the critical orifice to the sampling system as shown in Figure 16A-4 but without the  $\text{H}_2\text{S}$  cylinder. Connect a rotameter in the line to the first impinger. Turn on the pump, and adjust the valve to give a reading of about half atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable flow rate is reached, and record this as the critical vacuum. The measured flow rate

indicates the expected critical flow rate of the orifice. If this flow rate is in the range shown in Section 16.7.2, proceed with the critical orifice calibration according to Section 16.12.4.

16.7.5 Determination of Approximate Sampling Time. Determine the approximate sampling time for a cylinder of known concentration. Use the optimum sample volume obtained in Section 16.7.1.

$$\text{Approximate sampling time} = \frac{\text{Optimum volume}}{\text{Critical orifice flow rate}}$$

#### 16.8 Sample Collection.

16.8.1 Connect the Teflon tubing, Teflon tee, and rotameter to the flow control needle valve as shown in Figure 16A-4. Vent the rotameter to an exhaust hood. Plug the open end of the tee. Five to 10 minutes prior to sampling, open the cylinder valve while keeping the flow control needle valve closed. Adjust the delivery pressure to 20 psi. Open the needle valve slowly until the rotameter shows a flow rate approximately 50 to 100 ml above the flow rate of the critical orifice being used in the system.

16.8.2 Place 50 ml of zinc acetate solution in two of the impingers, connect them and the empty third impinger (dropout bottle) and the rest of the equipment as shown in Figure 16A-4. Make sure the ground-glass fittings are tight. The impingers can be easily stabilized by using a small cardboard box in which three holes have been cut, to act as a holder. Connect the Teflon sample line to the first impinger. Cover the impingers with a dark cloth or piece of plastic to protect the absorbing solution from light during sampling.

16.8.3 Record the temperature and barometric pressure. Note the gas flow rate through the rotameter. Open the closed end of the tee. Connect the sampling tube to the tee, ensuring a tight connection. Start the sampling pump and stopwatch simultaneously. Note the decrease in flow rate through the excess flow rotameter. This decrease should equal the known flow rate of the critical orifice being used. Continue sampling for the period determined in Section 16.7.5.

16.8.4 When sampling is complete, turn off the pump and stopwatch. Disconnect the sampling line from the tee and plug it. Close the needle valve followed by the cylinder valve. Record the sampling time.

16.9 Blank Analysis. While the sample is being collected, run a blank as follows: To a 250-ml Erlenmeyer flask, add 100 ml of zinc acetate solution, 20.0 ml of 0.01 N iodine solution, and 2 ml HCl solution. Titrate, while stirring, with 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  until the solution is light yellow. Add starch, and continue titrating until the blue color disappears. Analyze a blank with each sample, as the blank titer has been observed to change over the course of a day.

NOTE: Iodine titration of zinc acetate solutions is difficult to perform because the solution turns slightly white in color near the end point, and the disappearance of the blue color is hard to recognize. In addition, a blue color may reappear in the solution about 30

to 45 seconds after the titration endpoint is reached. This should not be taken to mean the original endpoint was in error. It is recommended that persons conducting this test perform several titrations to be able to correctly identify the endpoint. The importance of this should be recognized because the results of this analytical procedure are extremely sensitive to errors in titration.

16.10 Sample Analysis. Sample treatment is similar to the blank treatment. Before detaching the stems from the bottoms of the impingers, add 20.0 ml of 0.01 N iodine solution through the stems of the impingers holding the zinc acetate solution, dividing it between the two (add about 15 ml to the first impinger and the rest to the second). Add 2 ml HCl solution through the stems, dividing it as with the iodine. Disconnect the sampling line, and store the impingers for 30 minutes. At the end of 30 minutes, rinse the impinger stems into the impinger bottoms. Titrate the impinger contents with 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Do not transfer the contents of the impinger to a flask because this may result in a loss of iodine and cause a positive bias.

16.11 Post-test Orifice Calibration. Conduct a post-test critical orifice calibration run using the calibration procedures outlined in Section 16.12.4. If the  $Q_{\text{std}}$  obtained before and after the test differs by more than 5 percent, void the sample; if not, proceed to perform the calculations.

#### 16.12 Calibrations and Standardizations.

16.12.1 Rotameter and Barometer. Same as Method 11, Sections 10.1.3 and 10.1.4.

16.12.2  $\text{Na}_2\text{S}_2\text{O}_3$  Solution, 0.1 N. Standardize the 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution as follows: To 80 ml water, stirring constantly, add 1 ml concentrated  $\text{H}_2\text{SO}_4$ , 10.0 ml of 0.100 N  $\text{KH}(\text{IO}_3)_2$  and 1 g potassium iodide. Titrate immediately with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  until the solution is light yellow. Add 3 ml starch solution, and titrate until the blue color just disappears. Repeat the titration until replicate analyses agree within 0.05 ml. Take the average volume of  $\text{Na}_2\text{S}_2\text{O}_3$  consumed to calculate the normality to three decimal figures using Equation 16A-5.

16.12.3 Iodine Solution, 0.01 N. Standardize the 0.01 N iodine solution as follows: Pipet 20.0 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Titrate with standard 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the solution is light yellow. Add 3 ml starch solution, and continue titrating until the blue color just disappears. If the normality of the iodine tested is not 0.010, add a few ml of 0.1 N iodine solution if it is low, or a few ml of water if it is high, and standardize again. Repeat